conduction applicable to the drying of solids where internal diffusion controls led Boucher (3) to the conclusion that the extraction process was one of pure molecular diffusion. Since the importance of the process of diffusion in the extraction of actual materials has been questioned (6), a comparison was made between the extraction data on porous plates and on other materials. It is apparent that the results are comparable, and the effect of variables are the same. Diffusion, apparently, controls the entire process in the solvent extraction of the commercial oil-bearing materials.

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The Determination of Moisture in Tung Fruit[1]

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THE determination of moisture on materials containing tung oil is particularly difficult because of the tendency of tung oil to oxidize and increase in weight when heated. In this laboratory it has been standard practice to determine the moisture content of tung products by heating them in a vacuum oven for 2.5 hours at 101°C. under a vacuum of 12 mm. pressure. Such a procedure was used to minimize the error from the oxidation of the oil.

In 1948 the Subcommittee on the Analysis of Tung Fruit and Meal of the American Oil Chemists' Society adopted the procedure of drying the ground sample to constant weight at 101°C. in a forced draft oven as its tentative method for determining moisture in whole fruit (1). In collaborative work of this subcommittee no significant differences were found for the oil content of tung fruit when determined by different analysts, but significant differences in moisture content were found, indicating that the conditions specified for moisture determination were inadequate.

A comparison of the different methods for determining moisture was made on samples of fruit and seeds to determine their relative reliability and practicality.

All samples were ground through a Wiley[3] mill equipped with a 0.25-inch screen. For the finely ground samples the material which had been ground through the Wiley mill was reground through the Bauer[3] attrition mill with plates set at .008 inch. In the coarse grinding through the Wiley mill since the system is closed there is no appreciable loss of moisture, and the moisture content of the ground sample is considered to be the same as that of the original sample. Moisture is lost from the sample on fine grinding, and when oil is determined on the finely ground sample it is necessary to correct for this loss of moisture if the oil content of the original sample is required.

Methods Investigated

The methods studied were:

1. Drying in a forced draft oven to constant weight at 101-103°C. (1).
2. Drying in a vacuum oven under not more than 12-mm. pressure for 2.5 hours at 101-103°C. with no bleeding of air into oven.
3. Distilling with toluene (2).
4. Drying by hot air blower (Dietert Teller[3]) in which a large volume of heated air is blown through the sample held in a pan with a finely screened bottom (3). Air was blown through the sample for 15 minutes at 126.7°C.
5. Measurement of radio frequency impedance and correlation with moisture content (Steinlite Moisture Meter[3]) as determined by vacuum oven.
6. Titration with Karl Fischer reagent (6). Titrations were made in 40 x 120 mm. weighing bottles with standard ground outside tops using a magnetic stirrer. Electrodes were sealed into a top with a hole drilled through it to closely fit the burette tip.

Experimental Data

The results of moisture determinations on tung fruit and kernels, using the six different methods, are given in Table I. Comparisons were made between the first five methods on 34 samples. Subsequently comparisons were made between the vacuum oven and Karl Fischer methods for moisture determinations on 15 samples of fruit. All the data are shown in the same table.

Using the data in Table I, it cannot be shown that there are any differences in the comparative behavior of the different methods when used on the different materials (statistically, there is not a significant interaction between methods used and materials analyzed). Hence the results on all three materials can be averaged without obscuring any significant results, and only the means compared, provided for the means to be compared the same samples are averaged.

A statistical analysis of the data shows that the difference between the means for the vacuum oven and Karl Fischer methods is not significant. This is also true for the difference between the means for the distillation and forced draft methods. The mean of the values for the vacuum oven method is significantly higher than those for the distillation and forced draft oven methods, which in turn are significantly higher than the mean for the method using the hot air blower. The mean for the radio frequency meter was slightly but significantly lower than that for the vacuum oven method.

To study the effect of oxidation on apparent moisture content, percentages of moisture were determined

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[3]Mention of equipment by trade name does not constitute *endorsement* by the Department of Agriculture.

TABLE I

Average Percentage of Moisture in Tung Fruit, Seeds, and Kernels Determined by Different Methods

Material	No. of samples	Range of moisture[a]	Average percentage of moisture					
			Vacuum oven	Karl Fischer	Forced draft oven	Distillation	Hot air blower	Radio frequency impedance
Fruit	26	9.0-41.9	20.83	.....	20.22	20.02	19.43	18.90[b]
Fruit	15	3.8-26.6	13.23	13.44	.....	.....	.....	.....
Seeds	4	8.5-19.2	14.08	.....	13.32	13.62	12.58	12.65
Kernels	4	6.1-20.5	13.30	.....	12.82	13.02	12.35	13.27

[a] Determined by vacuum oven method.
[b] Based on 22 samples only. Corresponding average for determinations by vacuum oven method, 19.10%.

by heating ground samples of nuts in the forced draft oven for various periods as shown in Table II.

TABLE II

Percentage Moisture as Determined in Forced Draft Oven by Heating for Different Periods and the Resulting Error in Percentage of Oil[a]

Time of heating	Hulled nuts			50% Hulls and 50% Nuts		
	% Moisture		Error in % oil[b]	% Moisture		Error in % oil[b]
	Coarsely ground	Finely ground		Coarsely ground	Finely ground	
hrs.						
0.5	9.1	7.3	+.06	13.3	11.9	+.03
1.0	9.5	7.5	+.04	13.9	12.5	+.02
1.5	9.4	7.6	+.07	13.9	12.5	+.02
2.0	8.4	7.4	+.24	13.6	11.9	−.05
2.5	8.2	5.6	−.10	13.6	11.5	−.12
3.0	8.2	4.8	−.25	13.6	11.5	−.11
8.0	8.4	5.3	−.21	13.8	11.9	−.09

[a] The percentages of moisture as determined by drying in the vacuum oven for 2.5 hours at 101°C. were: hulled nuts, 10.1 for the coarsely ground sample and 8.0 for the finely ground sample; mixture of hulls and nuts, 14.8 for the coarsely ground sample and 13.3 for the finely ground sample.
[b] Calculated for 20% oil on coarsely ground sample, assuming that the percentages of moisture as determined in the vacuum oven are correct.

Discussion of Results

Vacuum Oven Method. The vacuum oven method has been used as standard by this laboratory with drying for 2.5 hours at 101°C. under a pressure of 12 mm. of mercury or less, with no bleeding of air through the oven.

That 2.5 hours' drying under the conditions used is enough is shown by the fact that 9 determinations on 3 different samples of coarsely ground material dried for 2.5 hours gave an average of 16.22% moisture while the average for the samples dried for 3.0 hours was 16.20, and corresponding determinations on the finely ground samples averaged 14.73% moisture for 2.5 hours and 14.69% for 3.0 hours. The vacuum was not broken during the drying period.

If many samples of high moisture content are put in the oven at the same time, the best procedure is to dry for 3.0 hours at 101° with a slight bleeding of air through the oven.

Forced Draft Oven Method. The lower moisture results obtained by drying in the forced draft oven in comparison with those obtained in the vacuum oven are readily explained. The prolonged heating of the sample in contact with a constantly changing layer of air produced oxidation of the oil, thereby increasing the dry weight and reducing the moisture values. Maximum moisture values are obtained at the point where the rate of loss of weight from evaporation of moisture becomes equal to the rate of gain in weight from oxidation. Beyond this point the apparent moisture values decrease, then as the heating is prolonged, they increase again.

The forced draft oven method was adopted for the determination of moisture in whole fruit by the Subcommittee on the Analysis of Tung Fruit and Meal of the American Oil Cheimsts' Society (1) although it was known that it gave results slightly low. However the only use made of the results obtained by the forced draft oven method has been in calculating the oil content of the finely ground samples of tung fruit to the basis of the original material.

Slight errors in the determination of moisture have no appreciable effect on the oil content calculated to the basis of the original sample, provided the errors on both the finely ground and coarsely ground samples are of the same order and in the same direction. Since the error results from the oxidation of oil in contact with the air, it would be expected that the finer the sample, the greater would be the error resulting from oxidation.

To check this, moistures were determined (in quadruplicate) on the ground samples by heating for different periods in the forced draft oven and by the vacuum oven method. The results are shown in Table II, along with the errors in the percentage of oil, when the moistures as determined in the forced draft oven are used to calculate the percentage of oil in the finely ground sample to the basis of the coarsely ground sample. Up to a heating period of 1.5 hours the error in the percentage of oil on the basis of coarsely ground sample is negligible, but for periods of heating longer than 1.5 hours the error may be as much as 0.2% on the hulled nuts.

The Tentative Method (Ad 2-48) of the American Oil Chemists' Society directs that the samples should be heated for one hour in the forced draft oven and then reheated for 30-minute periods until a loss of not more than 5 mg. on a 5-g. sample occurs during a 30-minute period. Unpublished data from routine moisture determinations show that one hour's heating is sufficient for the great majority of samples. After running a few samples in most cases, it will be found that the additional periods of heating can be omitted. These data also show that with long heating periods the finely ground samples oxidize more rapidly than the coarsely ground samples.

From an analysis of the foregoing and other results it seems that heating for one hour at 101°C. in a forced draft oven is about the optimum time for moisture determination on ground tung fruit although the exact time necessary would depend somewhat on the number of samples in the oven, the moisture content of the materials, the fineness of grinding, and the amount of air circulated.

Karl Fischer Method. Comparisons of moisture content, using the Karl Fischer and vacuum oven methods, were made on tung fruit that was about a year

old, and no difficulty was found in obtaining agreement between these methods when the Karl Fischer samples were digested in methanol for three hours at room temperature. When fresh fruit was used, digestion of the samples at room temperature gave low values for moisture content compared to the values obtained by the vacuum oven method. It was found necessary to digest the samples at 60°C. to dissolve all the moisture and obtain results comparable with those obtained by the vacuum oven method. Digestion at 60°C. has also been found necessary with some other types of materials (4).

To determine whether iodine was absorbed by the tung oil, titrations were made with the Karl Fischer reagent, using 10-g. samples of tung oil. An apparent moisture content of 0.07% was found for this oil. A trace of moisture would account for the value found, but even if it resulted from the absorption of iodine by the oil, the error on whole fruit would be negligible, *i.e.*, 0.01%.

Other Methods. Theoretically, of the methods studied, the toluene distillation and Karl Fischer methods should give most nearly the true moisture content because neither of these methods would be affected by the absorption of oxygen or the presence of volatile substances other than water to the extent that the oven methods would be. It is not possible to give a completely satisfactory explanation for the low values for moisture obtained by distillation with toluene as compared with the values obtained by the vacuum oven method. In the distillation method it is notoriously difficult to keep water from adhering to the glassware used. Either the distillation method gave low values because not all the water collected in the measuring tube, or the vacuum oven values are high because of the loss of volatile matter other than water. Because of the practical difficulties of accurately carrying out the distillation with toluene, the vacuum oven method is probably more reliable for routine moisture determinations.

Blowers in which a large volume of hot air is passed through the sample in a pan fitted with a fine-screened bottom have been used to considerable extent in the tung industry. McKinney (5) found that a correction of 1.20% should be added to values obtained when the moistures were determined in the blower by heating for 15 minutes at 126.7°C. The uncorrected values obtained with the blower are low because of oxidation, which also makes the values in the forced draft oven low. When a correction of 1.20% is added to the blower values, they are not significantly different from the values obtained in the vacuum oven method. The data in Table I actually indicate that a correction of 1.35% instead of 1.20% is needed to make the values obtained by the blower equal to the values obtained in the vacuum oven. Heating the samples for an additional 5 minutes decreases the percentage of apparent moisture on the average by 0.3%. The correction of 1.35% was determined on material ground through a 0.25-inch screen. Finer or coarser material might require a different correction.

The average moisture content of 30 samples as determined by the radio frequency impedance meter was 17.32% as compared to 17.66% for the average on the same samples by the vacuum oven method. This difference is small but significant. The standardization curves for the impedance meter were drawn by plotting the meter readings on a series of samples against the moisture content as determined by the vacuum oven method. Redrawing the curves to include the values obtained in preparing Table I would bring the results by these two methods into even closer agreement. Separate standardization curves had to be drawn for whole fruit, seeds, and kernels. The moisture content of two of the samples of whole fruit exceeded the range of the particular meter used (up to about 25% moisture). In practice, many samples of fruit would exceed this range, as much fruit is delivered to the mills with moisture content of 40 to 50%.

Summary and Conclusions

Six methods for determining moisture in tung fruit and seeds were compared.

The highest moisture values, and probably those most reliable, were obtained by drying the ground tung fruit in the vacuum oven at 101°C. for 2.5 hours under 12-mm. pressure, and by the Karl Fischer titration method. In using the Karl Fischer method on tung products, the sample must be digested in methanol at 60°C. Of these two methods the vacuum oven method is simpler and generally preferable.

Somewhat lower moisture values were obtained by the forced draft oven and toluene-distillation methods. The results obtained in the forced draft oven method were low because of oxidation of the oil in the samples. One hour at 101°C. in the forced draft oven seems to be the optimum time for moisture determination, and no appreciable error in the oil content results from using the percentages of moisture so determined to calculate the oil content to basis of sample as received.

For routine analysis, heating the ground tung fruit sample in a hot air blower for 15 minutes at 126.7°C. (260°F.) and adding a correction of 1.35% to the percentage of moisture obtained gives sufficiently accurate values for factory control purposes.

The radio frequency meter gave values close to those obtained in the vacuum oven method against which it was standardized. It was necessary to standardize the meter separately for fruit, seeds, and kernels. In practice many samples of wet fruit would be encountered which would exceed the range of the particular instrument used.

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